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(54) HIGH CORROSION RESISTANCE MOLYBDENUM-BASED COMPOSITE MATERIAL AND ITS PRODUCTION

(57)Abstract:
PROBLEM TO BE SOLVED: To impart a corrosion performance equal to that of Ta to a material and to obtain a mechanical strength and hardness more excellent than those of Ta by subjecting Mo and an Mo-based alloy to nitriding treatment.
SOLUTION: This high corrosion resistance Mo-based composite material is characterized by providing the surface of an Mo alloy with an Mo2N layer of 0.5 to 10 μm thickness. The method for producing a high corrosion resistance Mo-based composite material is characterized by subjecting an Mo series alloy to nitriding treatment for 0.2 to 100 hr in an atmosphere heated at a temp. of 700 to 1,150°C in the presence of gaseous N2 or gaseous NH3.

CLAIMS

[Claim(s)]
[Claim 1]A high-corrosion-resistance Mo system composite material providing a 0.5 micrometer - 10 micrometers-thick Mo_2N layer in the surface of Mo alloy.
[Claim 2]The high-corrosion-resistance Mo system composite material according to claim 1 using an Mo_2N layer as a beta-Mo $_2N$ layer.
[Claim 3]A manufacturing method of a high-corrosion-resistance Mo system composite material carrying out nitriding treatment of the Mo system alloy for 0.2 hour - 100 hours within atmosphere (700 ** - 1150 **) under existence of N_2 gas or NH_3 gas.
[Claim 4]A manufacturing method of a high-corrosion-resistance Mo system composite material providing an Mo_2N layer of thickness which carries out nitriding treatment of the Mo system alloy within atmosphere (700 ** - 1150 **) under existence of N_2 gas or NH_3 gas, and does not produce a crack at 0.5 micrometers or more in thickness.
[Claim 5]A manufacturing method of the high-corrosion-resistance Mo system composite material according to claim 4 thickness which does not produce a crack being less than 10 micrometers.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]It is related with a high-corrosion-resistance Mo system composite material, wherein this invention provides the Mo_2N layer which is high intensity and has Ta and the high corrosion resistance more than equivalent in the surface of Mo alloy, and a manufacturing method for the same.
[0002]
[Description of the Prior Art]As a high-corrosion-resistance material under conventionally severe conditions, the thing which carried out lining of Ta to the stainless steel container is known.
[0003]Three phases, gamma-Mo_2N (a face-centered-cubic system, fcc), beta-Mo_2N (considered a body center square system and bct), and delta-MoN (BI type of hexagonal hcp and a non-equilibrium phase), are among Mo metal dealt with by this invention as a nitride. However, a few [** et al. and in order that it may deal with it and these nitrides may not carry out ****** generation in easy pure N_2 gas / the research on Mo nitride]. Said parent phase is a phase stable only in a low temperature region 700 ** or less, and it is supposed that it is it the bct structure of having gamma-phase double C axial length. If gamma-phase has little nitrogen volume, it can obtain it from not less than 700 ** with quenching also in a presentation region. On the other hand, it is known that delta-MoN will be compounded by nitriding by NH_3 gas of MoO_3 or MoS_2. Although the crystal structure of this delta-MoN is made into the grating constant of a= 0.5725 micrometer, and c= 0.5608 micrometer of hexagonal system (hcp) structure, it is not known in detail. Thus, about Mo nitride, the details of those physical properties, a crystal structure, a generation temperature region, etc. are unknown, and the high corrosion resistance of the treatment object is not known at all.
[0004]
[The issue which it is going to solve by invention] Although Ta currently used actually has the performance which was excellent about corrosion resistance, a mechanical strength is low, wear and degradation are remarkable, and prolonged use is difficulty (there is no endurance).
And there were problems, like specific gravity is large, is expensive and there is.

[0005]Although it was known that surface nitriding of Mo system alloy can be performed, there was a problem that no it was known how it excels, what kind of the characteristic there is, or how it can be used.
[0006]
[Means for Solving the Problem]nitriding treatment of the Mo system alloy is carried out to a basis of appropriate alike conditions certain in this invention, and a film of nitriding Mo is provided in the surface.
Therefore, it excelled in corrosion resistance, a mechanical strength was large, and it succeeded in obtaining a cheap and lightweight composite material.

[0007]That is, an invention of material is a high-corrosion-resistance Mo system composite material providing a 0.5 micrometer - 10 micrometers-thick Mo_2N layer in the

surface of Mo alloy.
Let an Mo_2N layer be a beta-Mo $_2N$ layer.

[0008]An invention of process is a manufacturing method of a high-corrosion-resistance Mo system composite material carrying out nitriding treatment of the Mo system alloy within atmosphere (700 ** - 1150 **) under existence of N_2 gas or NH_3 gas for 0.2 hour - 100 hours. Next, other inventions of process carry out nitriding treatment of the Mo system alloy within atmosphere (700 ** - 1150 **) under existence of N_2 gas or NH_3 gas, It is a manufacturing method of a high-corrosion-resistance Mo system composite material providing an Mo_2N layer of thickness which does not produce a crack at 0.5 micrometers or more in thickness.
Thickness which does not produce a crack shall be less than 10 micrometers.

[0009]In said invention, if nitriding temperature exceeds less than 700 ** or 1150 **, an outstanding Mo_2N layer of the target corrosion resistance will not be made. When Mo_2N layer thickness is less than 0.5 micrometer, or also when exceeding 10 micrometers, it is difficult to acquire corrosion resistance made into the purpose of this invention. In the case of a beta-Mo $_2N$ layer, corrosion resistance excellent in authenticity is shown.
[0010]In the above, if ambient temperature exceeds 1200 **, an Mo_2N layer will not be formed, but this is presumed for decomposing. Since growth of an Mo_2N layer becomes remarkably slow in less than 700 **, ambient temperature is unsuitable to industrial production. For example, nitriding treatment was carried out at 700 **, and it has become clear that 100 hours or more are required for obtaining required thickness (1 micrometers or more).
[0011]In this invention, if treatment temperature is high, time into which an Mo_2N layer is grown up to predetermined thickness will become short, and if temperature is low, it will take long time. For example, although a 1-micrometer-thick Mo_2N layer could be obtained in 800 ** and 1 hour, it became a 12-micrometer-thick Mo_2N layer in 1000 ** and 1 hour.
[0012]Therefore, Mo_2N layer thickness is controllable by control of nitriding temperature and time.
[0013]
[Embodiment of the Invention]In this invention, nitriding treatment of the Mo system alloy is carried out.
Therefore, they are Mo system composite material which provided the 0.5 micrometer - 10 micrometers-thick Mo_2N layer in the surface of said Mo system alloy, or its manufacturing method.

[0014]Said Mo_2N layer has preferred beta-Mo $_2N$, and in order to grow up the thickness into 0.5 micrometer - 10 micrometers, 0.2 hour -100 time processing of it is carried out within atmosphere (700 ** - 1150 **).
[0015](Example 1 of an experiment) The green compact was produced by having made Mo powder and the TiC powder of the high grade into raw material, this was sintered in a 1800 ** hydrogen atmosphere, and the sintered compact was obtained. Between heat and warm rolling carried out this sintered compact, and the 1-mm-thick plate was further obtained through cold rolling. From this plate, the square-bar-like sample (2-mm^{W}x1-

mm^Ex25-mm^L) was started, and emery paper performed electrolytic grinding for the surface after polish. It recrystallized by 1500 ** and heat treatment of 1 hour in the vacuum (about 1.3×10^{-4}Pa) after that, and was considered as the sample for nitriding. Nitriding was performed in NH_3 gas air current of 1atm for 4 to 16 hours.
[0016]About the sample obtained with the above, the texture observation according a section after machinery polish and to an optical microscope and the hardness test (load 25gf, 15 s of maintenance periods) by a Vickers hardness tester were done. Etching for said observation by optical microscope is the Murakami reagent ($K_3[(Fe(CN)_6]$ it carried out using :NaOH:H_2 O= 1:1:10 (weight ratio).)). The X diffraction (XRD, Cu-Ka, Rigaku Geiger Flex) was performed for identification of the nitride layer of a specimen surface and an inside. Transmission electron microscope (TEM, Topcon EM-002B) observation and electron diffraction (ED) examined the fine texture of the nitride layer. After it used said sample for electron microscopes as the sheet metal of about 150-micrometer thickness by mechanical polish and it attached the hollow in the center of a sample by DIN PURA, it was produced using the ion milling system. Ion milling accelerated Ar^+ ion at 5-7 kV and 2 mA, and was performed by about 10-degree incidence angle.
[0017]As the sample obtained by said processing was shown in drawing 1, also in which sample, only the diffraction line of cubic (fcc) gamma-Mo $_2$N was accepted. This result shows that comparatively thick gamma-Mo $_2$N is formed in a specimen surface by nitriding.
[0018]The XRD pattern in the specimen surface which carried out 16 hour N_2 gas-nitriding processing of the Mo-Ti alloy at (a) 600 **-(f)1100 ** became like drawing 2.
[0019]Next, 1100 ** shows optical microscope **** of the section of 4 hours and the pure Mo sample [nitriding / for 16 hours / pure] to drawing 3 (a) and (b). Also in which sample, the white layer parallel to a specimen surface forms uniformly, and it turns out that the thickness of this surface layer is increasing with extension of nitriding time. If the result of said drawing 1 (b) is taken into consideration, it will be judged that this surface layer is an Mo nitride layer. It is dramatically smooth in the interface of this surface layer and internal Mo. Therefore, it is thought that most contribution of the grain boundary diffusion of nitrogen to growth of this surface layer cannot be found. This surface layer will be henceforth called a surface (Mo) nitride layer.
[0020]Generally, when such a compound layer grows, at the rate-limiting ceremony, two formulas can be considered by the difference in a rate-limiting mechanism. That is, in reaction rate-limiting rule, the thickness (E) of a compound layer is proportional to reaction time (t). The following straight-line rule type (1) is materialized.
[0021]
[Equation 1]

$$E = K_p \cdot t \quad \cdots\cdots \quad (1)$$

On the other hand, in the case of a diffusion limitation mechanism, the following parabola rule type (2) to which E is proportional to the square root of t is materialized.
[0022]
[Equation 2]

$$E = K_p \cdot t^{1/2} \quad \cdots\cdots \quad (2)$$

K_p is a growth rate constant here. Then, the relation of the square root of the nitriding time t is indicated to be thickness E of the surface nitride layer by 1100 ** nitriding of pure Mo of this invention, and Mo-0.5 Ti alloy to drawing 4. It turned out that straight-line relations are materialized among both and a parabola rule is materialized. The values of K_p of pure Mo and Mo-0.5 Ti alloy were $3.25 \times 10^{-4} mm's^{-1/2}$, and $2.96 \times 10^{-4} mm's^{-1/2}$ here, respectively. This result has suggested that rate-limiting [of the growth of a surface nitride layer] is seemingly carried out by the diffusion in Mo or the surface nitride layer of nitrogen.

[0023]Whether growth of a surface nitride layer advances toward the outside from a specimen surface or in order to examine whether it goes on toward the inside, Thickness W_b (here, the sample of 1000-micrometer thickness was used) and W_a before and behind nitriding were measured, and the change accompanying the nitriding time of the difference $**W=W_a-W_b$ was considered. The result is shown in drawing 5 about Mo-0.5 Ti alloy. the twice of the nitride layer which generated the sample thickness after nitriding like the case of pure nickel which oxidized above 1200 ** when growth of the surface nitride layer advanced by the outward growth by the diffusion to the specimen surface of Mo -- it is expected that the increase in thickness is carried out. However, as shown in drawing 5, it is shown that most thickness of a sample is not changing before and after nitriding, and the result with the same said of the case of pure Mo was obtained. Therefore, it is judged that growth of the surface nitride layer of this invention is for [inner] growth inside. Diffusion of nitrogen inside a sample concludes that growth of the surface nitride layer by NH_3 nitriding of pure Mo and Mo-0.5 Ti alloy is rate-limiting as aforementioned. This result is understood nitriding [without forming the void by the diffusion to the specimen surface of Mo ion] with Mo system material.

[0024]Next, the hardness distribution [nitriding / for 16 hours / distribution] of the section of the sample of pure Mo and Mo-0.5 Ti alloy is shown in drawing 6. Hv near the sample outermost surface is about 1800, and it turns out that it is remarkably high as compared with the hardness (Hv-200) of pure Mo before nitriding, and Mo-0.5 Ti alloy. The hardness of the surface nitride layer showed the tendency to fall to the inside of a nitrated case according to the other side. The fall of this hardness surmised that the phase change within a surface nitride layer was the cause. Then, about the sample [nitriding / for 16 hours / the sample], it was examined what the nitride would carry out the phase change toward the inside from the specimen surface. After grinding only predetermined thickness carefully in parallel and deleting it from a specimen surface toward an inside, operation of performing an X diffraction was repeated and, specifically, was performed. The result is shown in drawing 7 about pure Mo. The depth d= 0 (a) - near the specimen surface of 25(b) mum, it turns out to being cubic (fcc structure) gamma-Mo_2N (gamma-phase) that beta-Mo $_2$N (parent phase) of ****** is generating inside (d= 35 (c) - 70 (e) mum) from it. Furthermore, d= 80 micrometers (f) of an inside are a non-nitrated case, and only the diffraction peak of Mo was observed. The phase change of these Mo nitride is considered to bring about the difference in the hardness within a surface nitride layer. It was the same as that of the surface nitride layer of pure Mo also about the surface nitride layer of the Mo-0.5 Ti alloy.

[0025]Then, pure Mo is described below. The change accompanying the depth of the grating constant of the surface Mo nitride for which drawing 8 was asked from the result of the X diffraction is shown. Two results more interesting than drawing 8 were obtained.

The first, a grating constant changes discontinuously in a depth of about 28 micrometers in a surface nitride layer. From this result, though there is almost no field where gamma-Mo $_2$N by the side of the surface and beta-Mo $_2$N by the side of an inside live together or it is, it can be surmised that it is very narrow. It turns out that the grating constant of gamma-phase [near the surface] (d<30 micrometers) and the parent phase (d>30 micrometers) inside a nitride layer is changing to the second depending on both the sample depth, and a axial length gamma-phase in the other side and c axial length of a parent phase are short clearly inside a sample. As a result of asking for a grating constant according to an X diffraction about gamma-Mo_2N and beta-Mo_2N from which nitrogen volume differs by ****** (28.4at%-34.6%), it turns out that the grating constant (a gamma-phase a-axis, c axis of a parent phase) of these nitrides becomes short linearly with the fall of nitrogen volume. Therefore, it is thought that the phase change of Mo nitride within the surface nitride layer in this invention originates in the concentration change (inclination) of nitrogen in gamma-Mo_2N and a beta-Mo $_2$N phase.
[0026]According to drawing 9, when Mo nitride in a surface nitride layer changes from gamma-phase to a parent phase, structure will change from a cubic to ****** and the value of c/a will shift from 1. However, the axial ratio of a parent phase is changing from the result of drawing 9 within the limits of 0.966-0.953, and it can be regarded as the value near about 1. That is, it can be said that a parent phase is ****** near a cubic. c/a of a parent phase is examined paying attention to the lattice of Mo atom in a crystal structure. The mimetic diagram of the crystal structure of gamma-Mo_2N and beta-Mo $_2$N is shown in drawing 10 (a) and (b). The structure of the parent phase used the data of Evance ANDO jack (Evans and Jack) which can be trusted most. It can be considered that a gamma-phase structure is the structure with which the nitrogen atom trespassed upon the lattice position (8 face-piece crevice) of the fcc lattice which Mo atom constitutes. On the other hand, although the structure of a parent phase is a structure similar to gamma-phase, considering the unit cell of a crystal, a parent phase can be considered that c axis is fct short slightly (0.018 nm) compared with a and a b-axis. The axial ratio of a parent phase is about 1 from drawing 9. Therefore, in this invention, a parent phase presupposes henceforth that it is fcc structure approximately.
[0027]In said parent phase, as shown in drawing 11, many quenching organizations of gamma-Fe and same organizations like martensite are observed, and existence of countless stripes is accepted in Pando parallel to each other about 0.2 micrometer wide. It is thought that relaxation of the stress by the difference of a coefficient of thermal expansion between a surface Mo nitride layer and host phase Mo, the misfit of a lattice, etc. has taken place in this field. A part of result of having performed electron diffraction about this parent phase is shown in drawing 12 (a) and (b) with transmission electron microscope ****. In the incidence direction of an electron beam, all are [100] here. (a) of said drawing 12 and (b) are the diffraction patterns from the band area (inside a and b of a figure) which adjoins each other mutually, respectively. When both diffraction pattern is compared, it turns out that the adjacent bands have the same crystal orientation fundamentally. The streak which suggests existence of a tabular substance in the direction vertical to the stripes in a band is accepted into the diffraction pattern (b) from the band b. From this result, it is thought that the stripes in a band are trace of a plane defect vertical to a sample [100]. Trace analysis was conducted using the stereographic projection figure from the electron diffraction image of various directions about these

stripes. Drawing 13 (a) and (b) is a part of the result, (a) is [100] incidence and (b) is an analysis figure in [211] incidence. As a result, in [011] (the arrow showed in drawing 13), and the aforementioned [211] incidence, it turned out that the direction of striped is [1-31] in [100] incidence. Therefore, striped indices of crystal plane are contained in [011] zones and [1-31] zone, respectively, and striped indices of crystal plane exist on the great circle of the [011] zones shown in drawing 13, and the great circle of [1-31] zone. Drawing 14 shows that the indices of crystal plane common to both are {011}. That is, in (a) of drawing 12, in a field (0-11) and (b), it is a field (-101). It is thought that the stripes which exist innumerably in the band in a parent phase from the above examination are the plane defects on {011} sides vertical to {100} sides.
[0028]Next, the plane defect on the {011} sides of this parent phase is discussed. As a typical plane defect of an inorganic solid material, two kinds, a stacking fault and twin crystal, can be considered. The structure of a parent phase is fcc structure fundamentally, as shown in drawing 9 (b). It is necessary to consider the plane defect on {011} sides to this structure. Considering the atomic arrangement within a field, the method of lamination of {011} sides is the form of ABABAB.... that two kinds of lattice planes were mutually piled up as shown in drawing 14. The stacking fault in this structure produces lamination of AA or BB. Since this laminated structure produces very big strain energy, it can be said that the possibility of the stacking fault of {011} sides is very low.
[0029]Next, a possibility that the plane defect in a parent phase is the twin crystal which makes {011} sides a twin plane is examined. If the structure of a parent phase is the same cubic perfect fcc as gamma-phase, such twin crystal does not exist. No matter what lattice plane [which intersects perpendicularly with {011} sides] it may consider, it is because the lattice of the both sides has a reflectional symmetry relation mutually about {011} sides from the beginning. However, if ** et al. and the atomic arrangement of the field (011) of a parent phase whose parent phase is ****** with c axis short only slightly actually (c/a=0.966-0.953) are expressed typically, it will become like drawing 15 (a). In this atomic arrangement, if an atom is displaced merely slightly in the field top [0-11] direction as shown in drawing 15 (b) (011), the twin crystal (the amount s= 0.087 of shear strains) of [0-11] mold symmetrical (011) with reflection can be considered about a field (011). 2 phi since the field where a twin plane rotates the amount s of shear strains by this twin crystal by a field (011) and shear is a field (0-11) = it becomes 87.5 degrees and can be estimated as s= 0.087 from a formula (2.3). This value is remarkably small as compared with s= 0.077 in the above-mentioned {111} <112> type twin crystal. It has suggested that this result tends to produce the twin crystal of [(011) 0-11] mold. This type of twin crystal is actually observed by In which is fct metal only [in a pure metal]. From the above examination, it is thought in the parent phase of this invention that it was generated by the twin crystal of [(011) 0-11] mold. Then, it tried to carry out direct observation of such atomic arrangement by TEM. The high resolution electron microscope (HR-TEM) image of the parent phase photoed by one 550,000 times the magnification of this is shown in drawing 16. A sample face is the same (011) field as drawing 15 (a) and (b). A figure shows that the plaid of the field (020) of a parent phase and (002) a field is distorted considerably. However, atomic arrangement as shown in ** et al. and drawing 15 (b) was not accepted. When this observed a high-resolution image and it converged the electron beam, it turned out later that it originates in the organization of a parent phase collapsing easily by the damage by electron beam irradiation. Then,

magnification was lowered up to 83,000 times and photography on the conditions which lessened the damage by electron beam irradiation as much as possible was tried. The result is shown in drawing 17. A sample face is the same (100) field as drawing 15. [0-11] Existence of the plaid of the field which is in stripes with a width of about 10 nm extended in the direction mostly mutually at orthogonality relation (002) was accepted. Drawing 18 is the inverse Fourier transform image of the image which extended **** of drawing 17. The mimetic diagram of the twin crystal (011) of drawing 15 (b) is also united and shown for comparison. the angle of 87.7 degrees (calculated value) which the field in the mimetic diagram (002) of the twin crystal which the angle which the plaid of the field which is in orthogonality relation mostly mutually (002) which has appeared in the inverse Fourier transform image makes is about 87.5 degrees, and shows this angle below (011) makes -- about -- it turns out that I am doing one. From the above result, it was judged that the countless stripes looked at by drawing 17 were {011 <011>} type twin crystal which makes {011} sides a twin plane. From the above result, it became clear in the pure metal to be generated by the {011} <011> type twin crystal of the very new mold seen only by In also in a beta-Mo $_2$N nitride.
[0030](Example 2 of an experiment) The corrosion resistance of the product of this invention is explained. A sample is pure Mo produced with powder-metallurgy processing. The sample of the shape of a strip of paper the shape of a square of 10 mm squares or 2 mm in width, and 20 mm in length was started from 1 mm in thickness, and a 1.5-mm plate, and electrolytic grinding was performed after emery paper ground and removed the surface oxide film. About the strip-of-paper-like sample, it recrystallized by 1500 ** and heat treatment of 1 hour in the vacuum (about $1.3x10^{-4}$Pa) after that. 950 ** of nitriding was performed in NH_3 gas air current for 0.5 to 9 hours, and the sample was cooled by moving a sample to the greenhouse part of a work tube after nitriding.
[0031]a corrosion test uses a corrosion test instrument as shown in drawing 19 -- 40 - 75wt% -- it carried out for 3 minutes - eight days in boil sulfuric acid or 5 - 70wt% of nitric acid (ordinary temperature). The strip-of-paper-like sample which gave the square-like sample of 10 mm squares to the corrosion test in the inside of boil sulfuric acid, and performed recrystallization treatment to the corrosion test in the inside of nitric acid was used.
[0032]About the obtained sample, the surface state before and behind corrosion and the corroded condition of the section were observed using the scanning electron microscope (SEM, JEOL JSM6300) and the optical microscope. The X diffraction (XRD, Cu-Ka, Rigiaku Geiger Flex) was performed for identification of the specimen surface phase before and behind corrosion. The penetration rate (corrosion rate) computed the following formula using (3) from the weight change before and behind corrosion.
[0033]
[Equation 3]

$$\text{侵蝕度}\ (\mathrm{mm/year}) = \frac{(W_1 - W_2)}{d \times s} \times \frac{365 \times 24}{H} \times 10 \cdots (3)$$

however -- Weight before W_1:corrosion (g) Weight before W_2:corrosion (g) H:corrosion time d : density (g/cm^3) s: -- surface area (cm^2)
It comes out. The anticorrosion judging standard of the metallic material which is shown in Table 1 and which is generally used now was used for the anticorrosion judging

standard.
[0034]
[Table 1]

表1

腐食速度	評　価
<0.05	完全耐食性
0.05~1.0	耐食性あり
1.0>	耐食性なし

However, when this standard constitutes the manufacturing system of an industrial commodity to the last, it is a standard which noted whether being able to bear mechanically or not.
[0035]Therefore, when other factors become more important (for example, when contamination of the drugs by elution metal and a use schedule period are short etc.), it is necessary to use different standards according to each case. The concentration of sulfuric acid and the relation of the boiling point are as being shown in Table 2.
[0036]
[Table 2]

表2

H_2SO_4濃度(wt%)	加熱温度(沸点)(℃)
30	107.9
40	113.9
50	124.4
60	141.8
70	169.2
75	187.8
80	210.2
85	237.1
90	268.9
98.3	336.5
100	296.2

The corrosion rate of the various metal in the inside of boil sulfuric acid is shown in drawing 20. Pure Mo shows the outstanding corrosion resistance comparatively in 60% or less of low boil sulfuric acid of concentration. However, it turns out that corrosion resistance is lost quickly as concentration exceeds 60% and the oxidizing quality of sulfuric acid increases.
[0037]950 ** of SEM **** of the surface before and behind the corrosion test in various boil sulfuric acid of the sample [nitriding / for 9 hours / the sample] are shown in drawing 21 (a), (b), and (c). A test period is for eight days. Drawing 21 shows change not being observed in the state of a specimen surface before and after corrosion, and hardly being corroded with boil sulfuric acid also in 40% (a), 60% (b), and 75% (c) of which

concentration. This result has suggested that Mo nitride layer (Mo_2N) formed by NH_3 gas nitriding shows the corrosion resistance in which pure Mo was excellent as well as the low-density area also to boil sulfuric acid of not less than 60% of concentration region which loses corrosion resistance.
[0038]950 ** of corrosion rates in boil sulfuric acid of the sample [nitriding / for 9 hours / the sample] are shown in drawing 22. A solid line shows the corrosion rate of pure Mo for comparison. Drawing 22 shows that Mo nitride layer formed by NH_3 gas nitriding shows perfect corrosion resistance with 60% or less of sulfuric acid concentration. However, in ** et al. and 75% of sulfuric acid concentration, in spite of not having observed change in the state of the specimen surface at all (drawing 21 (c)), although it was about 1/20 of pure Mo, it became clear that corrosion advances at a remarkable speed (about 0.4 mm/y).
[0039]950 ** of thickness of the sample before and behind the corrosion of the sample [nitriding / for 9 hours / the sample] is shown in Table 3.
[0040]
[Table 3]

表3

		サンプル1	サンプル2
厚さ(mm)	処理前	1.417	1.423
	処理後	1.417	1.423

If the examination on the 8th is done with the corrosion rate of drawing 22, in the case of 75% of sulfuric acid concentration, sample thickness will decrease by about 18 micrometers in the rear surface sum total calculatively. However, it turns out that most thickness of a sample is not decreasing after [the examination for eight days in 75% sulfuric acid] ** et al. and Table 3. That is, it turned out that the corrosion of Mo nitride layer hardly advances also in 75% sulfuric acid.
[0041](a) which shows drawing 23 (a) and (b) 950 ** of optical microscope **** of the specimen surface before the corrosion of the sample [nitriding / for 9 hours / the sample] is a sample of 10 mm squares, and (b) is the strip-of-paper-like sample which performed recrystallization treatment before nitriding. It turns out that the crack considered to have generated (a) and (b) in the specimen surface after nitriding from this by distortion produced during sample cooling exists (a figure Nakaya seal shows). Along the grain boundary of Mo nitride, these cracks do not exist then, and have run through and spread the inside of the grain of a nitride so that clearly from drawing 23 (b). Therefore, the crack has attained that corrosion advances although there is no change in the sample thickness before and behind corrosion to the interface of a nitride layer and host phase Mo.
It is thought that it is because Mo of a host phase is selectively corroded at the tip of a crack.

[0042]Optical microscope **** of the section of a sample (b) which did the corrosion test for eight days in (a) and 75% boil sulfuric acid before corrosion is shown in drawing 24. As a figure Nakaya seal shows, the crack generated in Mo nitride layer has run through the nitride layer thoroughly, and as for the tip, signs that only Mo of the host phase was corroded selectively are observed clearly. If drawing 24 (a) and (b) is compared, change

will be observed in neither the thickness (about 30 micrometers) of a nitride layer, nor the width of a crack before and after corrosion of after the examination for eight days, Not being corroded sets most Mo nitride layers to understand (drawing 24 (b)), and the nitride layer surface looks unevenly because the nitride was missing and fell by polish.
[0043]Although Mo nitride layer formed by NH_3 gas nitriding shows very good corrosion resistance to boil sulfuric acid by the above result, As a result of a sulfuric acid solution's contacting a host phase through the crack considered to generate by distortion produced during sample cooling, it became clear that the alternative corrosion of Mo advances by the tip part of a crack in the high-density area from 60% in which Mo loses corrosion resistance. Therefore, in order to use Mo nitride layer as a corrosion resistant material, it is indispensable to suppress generating of a crack thoroughly.
[0044]It is known that strain energy in case a crystalline substance grows as a tunic after other crystals will generally increase in proportion to thickness. Then, since strain energy was low stopped when shortening nitriding time and making thickness of Mo nitride layer thin, I thought that generating of the crack under cooling was controllable. Optical microscope **** of the surface of the sample which carried out 1 hour (a) and 0.5-hour (b) nitriding of the recrystallization material at 950 ** is shown in drawing 25. The thickness of the nitride layer generated by nitriding of 9 hours by drawing 24 is about 30 micrometers. Therefore, if it thinks that the parabola rule of (2) types is materialized about growth of Mo nitride layer by NH_3 gas nitriding, the thickness of the nitride layer generated by nitriding of 950 **, 1 hour, and 0.5 hour will be estimated at 10 micrometers and 7 micrometers, respectively. As opposed to generating of a crack being observed in the portion still shown by an arrow when nitriding time is 1 hour (a), Therefore generating of the same crack was not accepted, the lamination of Mo nitride layer by shortening of nitriding time became clear [a very effective thing] to control of a crack generation in 0.5 hour (b).
[0045]The XRD pattern of the surface of 9-hour nitriding material (a), 1-hour nitriding material (b), and 0.5-hour nitriding material (c) is shown in drawing 26. Although a gamma-phase diffraction line is slightly accepted by nitriding material (c) for 0.5 hour for 9 hours to the surface layer of nitriding material (a) and 1-hour nitriding material (b) being gamma-Mo_2N, it turns out that the main is a parent phase. The nitride which generates this result in early stages of nitriding is a very important result also at the point which has suggested that it is a parent phase. It is because that the diffraction line of Mo is accepted by drawing 26 (c) has the thin thickness of Mo nitride layer. Although the cause by which generating of a crack is controlled in nitriding material for 0.5 hour is considered to be because for the nitride layer to be thin, distortion may have been eased with the {011} twin crystal by which it is generated in a parent phase, and it is a future examination technical problem.
[0046]The value of pure Mo is also united and shown in Table 4 for comparison which shows the corrosion rate in the inside of 75% boil sulfuric acid of 9-hour nitriding material and 0.5-hour nitriding material, and the sample thickness before and behind nitriding. Comparison of the corrosion rate in the inside of 75% sulfuric acid of 9 hours (b) and 0.5 hour (c) nitriding material is illustrated at 950 ** among Mo [nitriding] material (a) NH_3 gas to drawing 27. As a result of suppressing generating of a crack by shortening nitriding time and making a nitride layer thin, the corrosion rate of nitriding material falls for 9 hours for 0.5 hour to about 1(about 1/60 of Mo)/3 of nitriding material,

the lamination of a nitride layer is remarkable and an effect is accepted. However, it turns out that the sample thickness of nitriding material is completely changeless before and behind corrosion for 0.5 hour, and corrosion is still advancing in spite of also considering a beta-Mo $_2$N phase that ****** corrosion resistance is shown like gamma-phase [of nitriding material] for 9 hours.
[0047]Optical microscope **** of the surface of the 0.5-hour nitriding material which did the corrosion test for five days in 75% boil sulfuric acid is shown in drawing 28. When the sample after corrosion was carefully observed to a crack not being observed in the 0.5-hour nitriding material before corrosion (drawing 25 (b)), it became clear that the crack has occurred as an arrow shows. Considering that Mo nitride layer is hardly corroded, these cracks, Such a thin crack exists from before corrosion, it is hard to think that this spread by corrosion, therefore as a result of these cracks' occurring slightly during a corrosion test, it is thought that it does not understand in observation by optical microscope that corrosion advanced at the speed seemingly shown in Table 4. It is known well that austenitic stainless steel will generate stress corrosion cracking in a chloride. Although the same phenomenon may have happened also in the 0.5-hour nitriding material of Mo of this invention, it is necessary to perform remaining stress measurement etc. for details from now on, and to clarify.
[0048]here, the surface Mo nitride layer was markedly boiled rather than the case of 950 ** and 0.5-hour nitriding among NH_3 gas, and it was made thin in order to control generating of a crack, and aiming at improving corrosion resistance by leaps and bounds, nitriding at 800 ** was tried among N_2 gas. 800 ** of XRD patterns of the surface of the material [nitriding / for 48 hours / material] are shown in drawing 29 among N_2 gas as one of them. The diffraction peak of beta-Mo $_2$N other than the strengthening diffraction peak of Mo is observed clearly, and formation of very thin beta-Mo $_2$N it is guessed that is about about 0.5-1 micrometer is suggested. The result of the corrosion test in the 75% concentrated-sulfuric-acid solution of this nitriding material is shown in drawing 27. It found out that the corrosion rates of the 800 ** nitriding material in N_2 gas were 0.02 mm/y, their corrosiveness improved among NH_3 gas by leaps and bounds than 950 ** and 0.5-hour nitriding material, and perfect corrosion resistance was shown also in a 75% sulfuric acid solution with this figure. That is, it was specified by making very thin Mo nitride layer form in a material-list side that Mo system composite material which has **** high corrosion resistance also in a boil concentrated-sulfuric-acid solution is producible.
[0049]
[Table 4]

表4

時 間		9時間		0．5時間		純Mo
区 分		ｻﾝﾌﾟﾙ1	ｻﾝﾌﾟﾙ2	ｻﾝﾌﾟﾙ1	ｻﾝﾌﾟﾙ2	
腐食率(mm/year)		0.4283	0.4054	0.1309	0.1270	~8.0
厚さ(mm)	処理前	1.417	1.423	1.876	1.855	−
	処理後	1.417	1.423	1.875	1.855	−

The corrosion rate in the inside of boil nitric acid of various refractory metals is shown in drawing 30. Although Ta, Nb, and Zr show good corrosion resistance by total

concentration, Ti and W show the tendency for a corrosion rate to become large a little with intermediate density.
[0050]Pure Mo (a) and 950 ** show the corrosion rate in the inside of nitric acid in the ordinary temperature of the sample (b) which performed the nitriding material of 9 hours to drawing 31. Unlike other refractory metals shown in drawing 30, since pure Mo (a) has the small passivation ability to nitric acid, also in ordinary temperature, it is corroded at a remarkable speed. When nitric acid concentration exceeds 10%, it stops showing corrosion resistance at all, and near 50% of concentration shows the maximum. It was 5% or less of nitric acid concentration that pure Mo shows perfect corrosion resistance at ordinary temperature. On the other hand, in the case of the sample (b) which performed nitriding of 9 hours, the tendency is the same as that of pure Mo, but it turns out that the corrosion rate (about 0.33 mm/y - 240 mm/y) in 10% - 50% of concentration region is smaller than pure Mo (about 3 mm / 10 ^{4}mm/y) single or more figures. By the nitriding material of 9 hours, the crack as shown in drawing 22 exists, and if it takes into consideration that Mo is corroded in the tip part of a crack, the corrosion rate of Mo nitride layer will be considered to be actual smaller. However, ** et al., the SEM **** twist before and behind corrosion in 50% nitric acid of the nitriding material of 9 hours shown in drawing 32, It turns out that Mo nitride layer is also being corroded extensively (**** (b)), therefore in order to raise the corrosion resistance of Mo nitride layer to nitric acid, it is thought that alloying with other passive state type metal is required.
[0051]Next, the corrosion resistance which it is under [solution-of-hydrochloric-acid] receiving was examined. Comparison of the corrosion rate in the inside of the solution of hydrochloric acid of various metal is shown in drawing 33. Ta, W, Mo, and Zr are excellent in corrosion resistance as compared with other metal. 950 ** shows comparison of the corrosion rate in the inside of the 35% solution of hydrochloric acid of the nitriding material of 9 hours to drawing 34 among Mo [nitriding] material and NH_3 gas. The beta-Mo $_2$N phase forms this nitriding material in a specimen surface comparatively thickly like the above-mentioned (drawing 23, 24, 25, 26). although Mo [nitriding] material shows corrosion rate:0.0059 mm/y and the outstanding corrosion resistance from drawing 34, it turns out that nitriding material is boiled markedly and its corrosion resistance is improving rather than this Mo material. That is, the corrosion rate of nitriding material decreased to about 1/5 of 0.0011 mm/y and Mo [nitriding] material, and having **** high corrosion resistance was found out.
[0052]Subsequently, in order to examine the corrosion resistance in the alkaline solution of Mo system material, the corrosion test in a sodium hydroxide solution was done. One example of a result is shown in drawing 35. Drawing 35 shows 950 ** of comparison of the corrosion rate in the inside of the 20% sodium hydroxide solution of the material [nitriding / for 9 hours / material] among Mo [nitriding] material and NH_3 gas. Although Mo [nitriding] material also showed corrosion rate 0.0020 mm/y and perfect corrosion resistance, with nitriding material, it turned out that a corrosion rate shows 0.0015 mm/y and the corrosion resistance superior to Mo [nitriding] material is shown.
[0053](Example 3 of an experiment) Optical microscope **** [nitriding / **** / drawing 36] of the section of pure Mo (a) and Mo-1.0 Ti alloy (b) is shown. After carrying out resin embedding of the section, mechanical polish was performed, and it buffed using diamond slurry with a particle diameter of 1 micrometer after that. Also in which sample, generation of a surface nitride layer about 80 micrometers thick is

observed in the surface. At pure Mo (drawing 36 (a)), the difference clearer than a surface nitride layer in the polish state of an internal organization is accepted by Mo-1.0 Ti-alloy drawing 36 (b) to a difference not being observed in the polish state of an internal organization from a surface nitride layer. In the field from the interface of a surface nitride layer and a host phase to about 200 micrometers, since hardness is higher compared with an inside than compared with it, polish speed serves as little late concavo-convex flat organization. It is an internal nitride layer considered that were nitriding [dissolution Ti] preferentially and detailed Ti-nitrides particles carried out dispersed precipitation of this field. Even when nitriding [Mo-1.0 Ti alloy / with NH_3 gas], generating of the crack was similarly observed in the surface nitride layer. The hardness distribution [nitriding / distribution / drawing 37] of the section of a pure Mo (a), Mo-0.5Ti (b), and Mo-1.0Ti (c) alloy is shown. The depth from the surface corresponds to the Mo_2N surface nitride layer which the high hardness field (Hv-1700) up to about 80 micrometers showed to drawing 30. When nitriding [Mo-Ti alloy] ((b), (c)), an internal nitriding layer with high hardness of a surface nitride layer which is not immediately seen inside in the case of pure Mo is formed. Directly under a surface nitride layer, Hv shows the high value of 800-980, and the hardness of this field decreases gradually toward an inside. The maximum of the hardness within an internal nitriding layer is Hv-980 in Hv-800 and Mo-1.0 Ti alloy at Mo-0.5 Ti alloy, and is dependent on Ti quantity. It is guessed that the high hardness within this internal nitriding layer is what is depended on dispersion strengthening of detailed Ti-nitrides particles.

[0054]About strengthening of Mo alloy by particle distribution, the research which distributed the TiC particle by the mechanical alloying (MA) method is known. Although the maximum hardness in this alloy shows Hv - 500, in addition to strengthening by a TiC particle (1wt%), it includes work hardening by MA in this value. On the other hand, the point which strengthening in the internal nitriding layer in this invention is purely based on dispersion strengthening of Ti-nitrides particles excluding work hardening, and shows remarkable strengthening in few amount of Ti nitrides is the big feature.

[0055]The depth from which hardness serves as the maximum in Mo-0.5Ti [nitriding / Ti / drawing 38] (a), and the internal nitriding layer of an Mo-1.0Ti (b) alloy (in Mo-0.5Ti, about 80 micrometers) In any case, in Mo-1.0Ti, the incidence direction of the O electron line which shows transmission electron microscope **** in about 130 micrometers is parallel to [001] of host phase Mo. Signs that many particles (long and slender white portion of the center of a distorted place) with a distorted place (it corresponds to a black portion) are carrying out dispersed precipitation are observed clearly. Since the streak was accepted in the vertical direction to the particles extended in the <100> directions of a host phase by the result of electron diffraction, it turned out that these Ti-nitrides particles deposit as tabular particles on the {100} sides of host phase Mo. That size is a very detailed and overly laminated particle (about 2-4 nm in width, and about 0.45 nm in thickness), and it is thought that this particle is Ti nitrides (TiN). About 0.45 nm in thickness of a sludge is a size (a_{TiN}=0.424nm) of one unit cell of TiN here. As for deposit distribution of such overly laminated particles, a metallic material besides the former does not almost have an example of a report.

compared with the Mo-0.5 Ti alloy (a), hardening in an internal nitride layer had a distorted place from these results with more [the Mo-1.0 Ti alloy with much Ti quantity (b)] deposit particles -- the dispersed precipitation of detailed Ti nitrides is overly judged

to be the cause.
[0056]HR-TEM image (a) and its inverse Fourier transform (IFFT) image (b) of the sludge distributed in the internal nitriding layer are shown in drawing 39. A sample face is a field like drawing 32 (001), and can be seen. [of the plaid of the field (110) of a host phase and (1-10) the field] In the image (b) which expanded the particles shown by ** in drawing 39 (a), and performed inverse Fourier transform, the remarkable lattice strain was observed in the circumference of the sludge. However, the host phase and the lattice are connected and ** et al. and these sludges keep compatibility perfect. The rearrangement by the misfit of the lattice of a host phase and a sludge is not accepted. Since the solute element is Ti, it is thought that a sludge is TiN of fcc structure. When this TiN particle deposits on the {100} sides of host phase Mo (bcc), the orientation relationship whose misfit decreases most from each grating constant being a_{Mo}=0.314 [nm] and a_{TiN}=0.424 [nm] is a relation of a following formula as shown in drawing 40.
[0057]
[Equation 4]

$$(100)_{Mo} \ // \ (100)_{TiN} \quad \cdots\cdots \quad (4)$$

[0058]
[Equation 5]

$$[100]_{Mo} \ // \ [100]_{TiN} \quad \cdots\cdots \quad (5)$$

This relation is a relation of BAKKA Nutting (Backer-Nutting) often [in the case of the sludge in a gamma-Fe system alloy (bcc)] seen, and same relation. This orientation relationship is in agreement also with the result of having performed internal nitriding at 1300 ** in pure nitrogen, in Mo-Ti alloy.
[0059]While TiN keeps compatibility perfect with a host phase, when it deposits, the maximum size of the diameter D and thickness t is considered to be the following formula (6) and (7) which becomes equal to interval deltaD and deltat of a misfit rearrangement.
[0060]
[Equation 6]

$$\delta D = d^2_{(200)TiN} / \varepsilon_1 \quad \cdots\cdots \quad (6)$$

[0061]
[Equation 7]

$$\delta t = d^2_{(200)TiN} / \varepsilon_2 \quad \cdots\cdots \quad (7)$$

It is epsilon$_1$=$|d_{(220)\,Mo}-d_{(200)\,TiN}|$ and epsilon$_2$=$|d_{(200)\,Mo}-d_{(200)\,TiN}|$ here. Therefore, size of TiN which can deposit while maintaining compatibility if it calculates by substituting $d_{(200)\,Mo}$=0.15nm, $d_{(220)\,Mo}$=0.222nm, and $d_{(200)\,TiN}$=0.212nm for an upper type [0062]
[Equation 8]

$$直径\ D \sim 4.5 \ [nm] \quad \cdots\cdots \quad (8)$$

[0063]
[Equation 9]

厚さ $t \sim 0.45$ [nm] ...... (9)

It can estimate. The deposit sizes seen by this invention are about 2-4 nm in width, and 0.45 nm in thickness as mentioned above, and this observed value is mostly in agreement with the calculated value of a formula (6.7). Therefore, within the internal nitriding layer at the time of nitriding [1100 **], it is thought that TiN for thickness 1 unit (0.424 nm) maintains compatibility, and deposits.

[0064]In the Mo-1.0 Ti alloy [nitriding / the Ti alloy], direct observation of the detailed distribution of the sludge in the various depth in an internal nitriding layer was carried out by TEM. In any case, the incidence direction of an electron beam is parallel to host phase Mo [001] like drawing 38. As for drawing 41 (a), (b), and (c), depth d from the specimen surface of Mo-1.0 Ti alloy corresponds to d= 130 micrometers, the position of the maximum (-980), the position that decreased to the interim value (-700), and the position which decreased to the value (-310) near the value of a host phase, respectively. It became clear that the density of TiN sludge particles decreases as it fell like the position inside these **** twists and a sample (i.e., hardness). It also turned out that most sizes of the sludge particle change. Therefore, it seems by field drawing 41 (b) and (c) with low hardness that dissolution Ti still exists considerably.

[0065]The relation of the square root (N) of the distribution density of TiN sludge particles and the ascending amount (**Hv) of hardness which were measured from **** of the TEM observation of drawing 41 is shown in drawing 42. **Hv is a difference of hardness $(Hv)_{matrix}$ of hardness Hv host phase Mo in each depth here. Jam, [0066]

[Equation 10]

$$\Delta Hv = Hv - Hv_{matrix} \quad \cdots\cdots \quad (10)$$

It turns out that **Hv is proportional to the square root of N from this. namely[0067]

[Equation 11]

$$\Delta Hv \propto N^{1/2} \quad \cdots\cdots \quad (11)$$

If it approximates with a cube by making shape of a sludge into the first approximation here, the volume fraction (f) can be expressed with the following formulas using the number (n) of the particles contained volume (V) of a host phase, a particle size (r), and in it.

[0068]

[Equation 12]

$$f = nr^3 / V = r^3 N \quad \cdots\cdots \quad (12)$$

In an upper type, consideration of the result change was not accepted to be to the size of the sludge within the internal nitriding layer in the TEM observation of drawing 41 can consider that size r of a sludge is fixed. In this case, the following relations are obtained between f and N.

[0069]

[Equation 13]

$$f \propto N \quad \cdots\cdots \quad (13)$$

A formula (13) and a formula (11) show that **Hv is proportional to the square root of

the volume fraction f of TiN sludge particles. namely[0070]
[Equation 14]

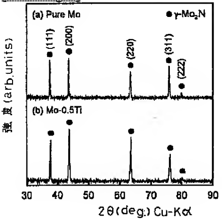
$$\Delta Hv \propto f^{1/2} \quad \cdots\cdots \quad (14)$$

From the above examination, reduction of the depth direction of **Hv within an internal nitriding layer became clear [that he can understand by reduction in the depth direction of the volume fraction of TiN particles], as shown in a formula (14).
[0071]If it roughly divides about the mechanism of strengthening in case the 2nd phase deposits by nitriding, two kinds of mechanisms can be considered. That is, the shearing-machine style of the sludge by rearrangement in which a sludge is small and a rearrangement is able to pass a sludge, and a sludge are large, and when a rearrangement bypasses a sludge, the dislocation loop which it leaves to the circumference of a sludge is two kinds of OROWAN mechanisms used as the resistance force of movement of the next rearrangement. In the case of the shearing-machine style by the rearrangement of detailed deposit particles with consistency distortion, it is known experimentally that **Hv is proportional to the square root of the volume fraction of a sludge. It is thought that the sludges in this invention are the very small and thin particles which maintained a host phase and compatibility, and passage of a rearrangement is possible for them enough, If the proportionality between **Hv of a formula (14), and $f^{1/2}$ is taken into consideration, it will be judged that the mechanism of strengthening of the internal nitriding layer by nitriding at 1100 ** is a shearing-machine style of the sludge by rearrangement.
[0072]If the nitriding [Mo-Ti alloy] using NH_3 gas as explained above, an internal nitriding layer with high phase hardness conjectured to be based on the dispersed precipitation of detailed TiN particles will be formed in an inside from a surface Mo nitride layer. Although the hardness within an internal nitriding layer showed the maximum directly under the surface nitride phase and used it as the inside beyond, it decreases gradually. as for the maximum of the hardness of an internal nitriding layer, Hv-980 and the direction with much Ti quantity which comes out and exists are hard with Hv-800 and Mo-1.0 Ti alloy with the Mo-0.5 Ti alloy.
[0073]
[Example]The material of the Mo-0.5wt% Ti alloy created by powder metallurgy was rolled, and the place and the 7-micrometer-thick beta-Mo $_2$N layer were obtained. [nitriding / in NH_3 gas air current of 1atm / the cut square-bar-like sample (2mmx1mmx25mm) / the layer / for 0.5 hour / 950 **] After being immersed in dilute sulfuric acid for one week by making these processed goods into a corrosion test, it took out and observed, but corrosion was not found. The hardness in this case was Hv-800. The hardness of pure Mo is Hv-200.
[0074]
[Effect of the Invention]Since this invention carried out 0.2 hour -100 time processing of Mo or the Mo system alloy within atmosphere (700 ** - 1150 **) and 0.5 micrometer - 10 micrometers of Mo_2N layers provided it in the base material surface, Corrosion resistance is raised by leaps and bounds, and from Ta, it improves remarkably and hardness is ****(ed) with Ta in anticorrosion performance, mechanical strength is large, it is lighter-weight than Ta and there are several effects, like a price is also cheap and

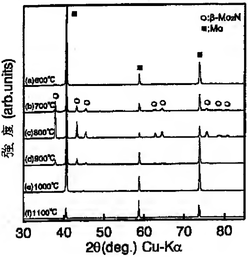
there is.

DRAWINGS

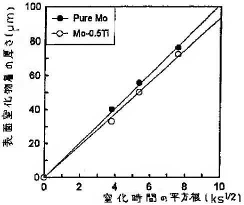
[Drawing 1]



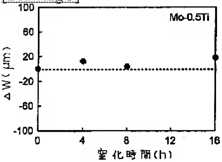
[Drawing 2]



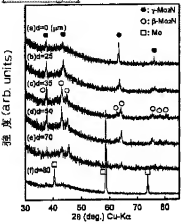
[Drawing 4]



[Drawing 5]

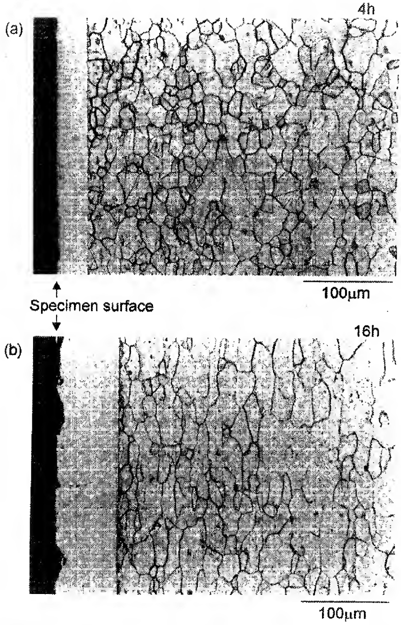


[Drawing 7]



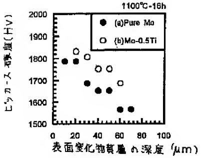
[Drawing 3]

図面代用写真



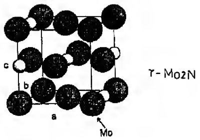
Specimen surface : 試料表面

[Drawing 6]

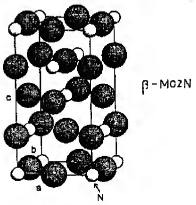


[Drawing 10]

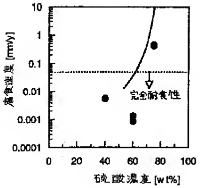
(a)



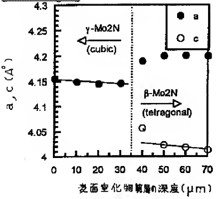
(b)



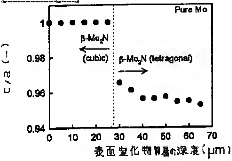
[Drawing 22]



[Drawing 8]

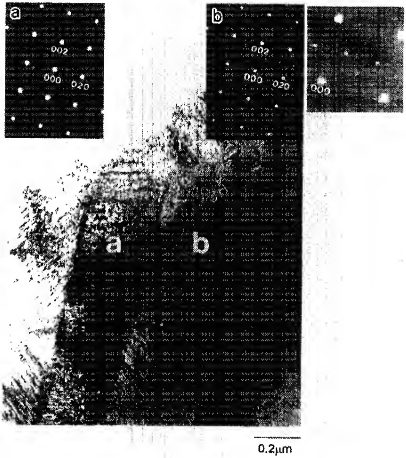


[Drawing 9]

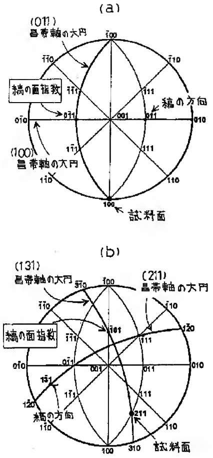


[Drawing 12]

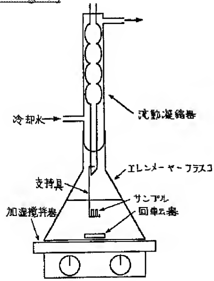
図面代用写真



[Drawing 13]



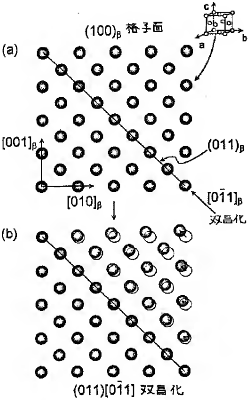
[Drawing 19]



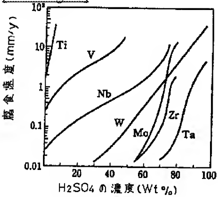
[Drawing 11]

図面代用写真

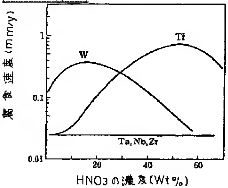
[Drawing 15]



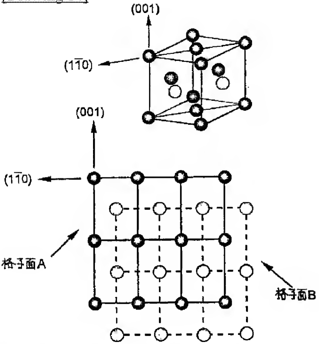
[Drawing 20]



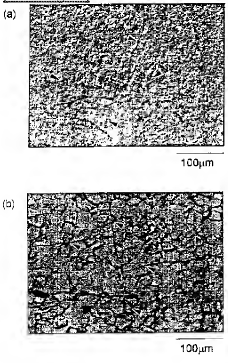
[Drawing 30]



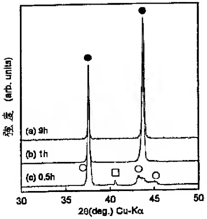
[Drawing 14]



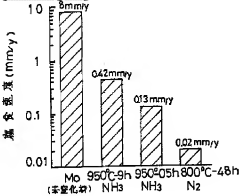
[Drawing 23]



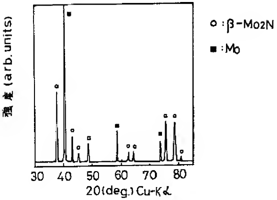
[Drawing 26]



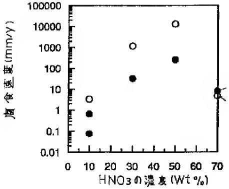
[Drawing 27]



[Drawing 29]

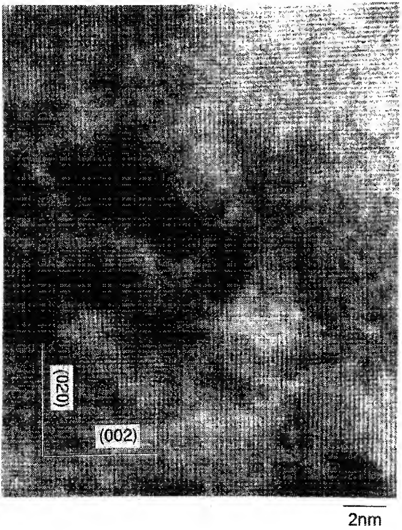


[Drawing 31]

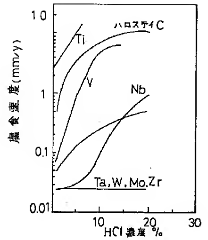


[Drawing 16]

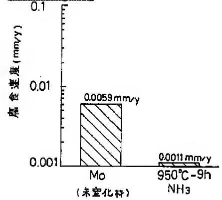
図面代用写真



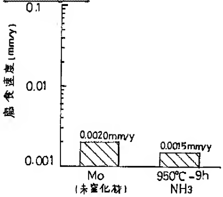
[Drawing 33]



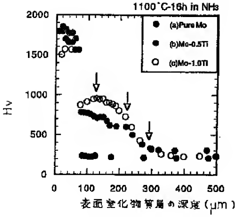
[Drawing 34]



[Drawing 35]

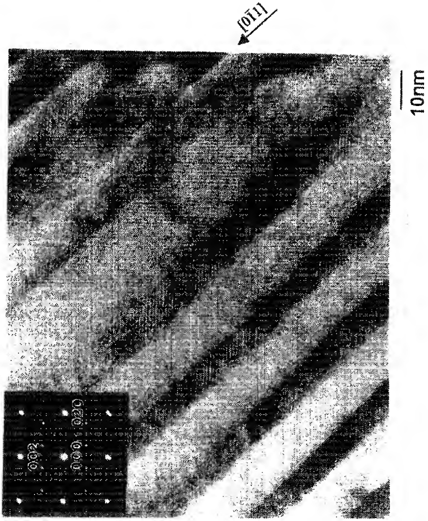


[Drawing 37]

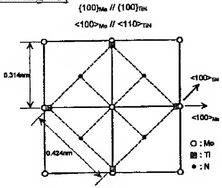


[Drawing 17]

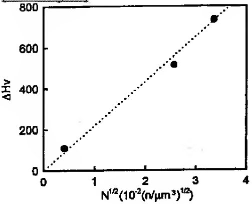
図面代用写真



[Drawing 40]



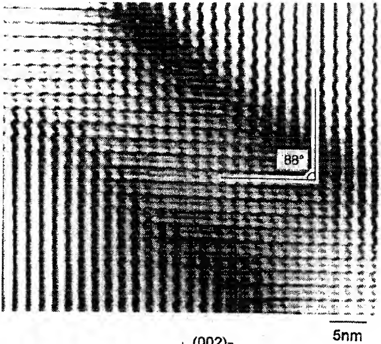
[Drawing 42]



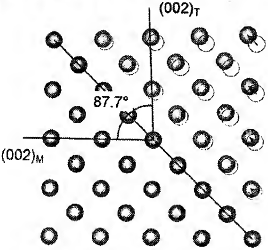
[Drawing 18]

図面代用写真

(a)

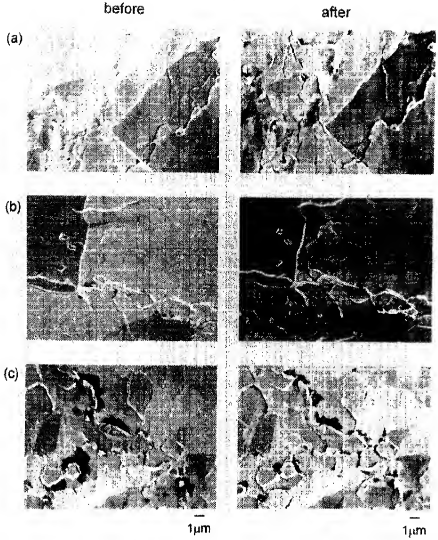


(b)



[Drawing 21]

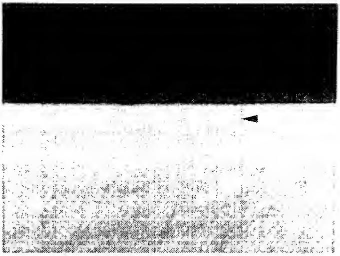
図面代用写真



[Drawing 24]

図面代用写真

(a)



100μm

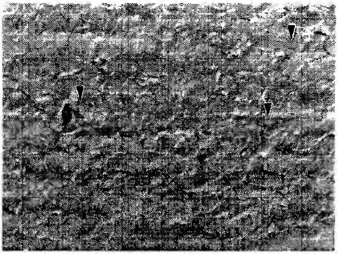
(b)

100μm

[Drawing 25]

図面代用写真

(a)



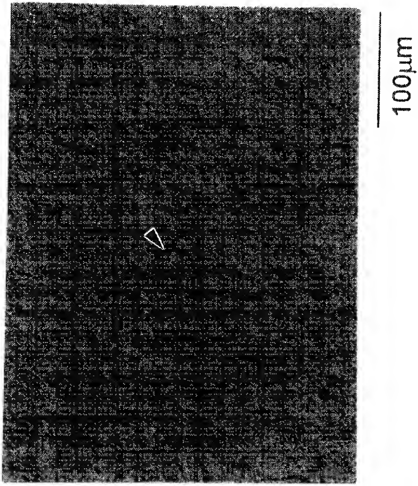
100μm

(b)

100μm

[Drawing 28]

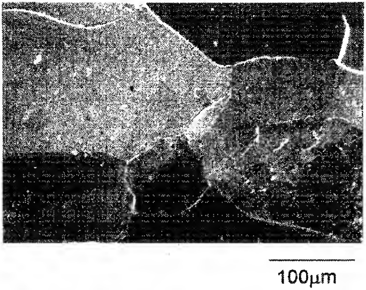
図面代用写真



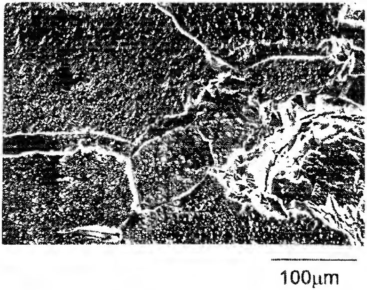
[Drawing 32]

図面代用写真

(a)



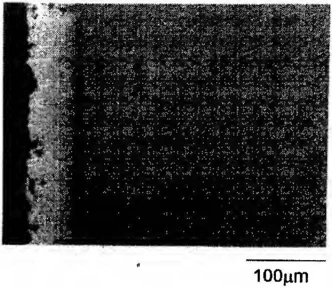
(b)



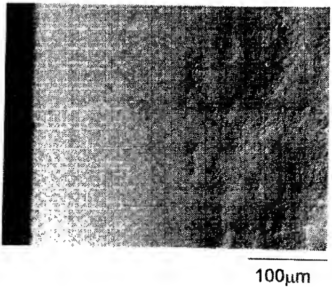
[Drawing 36]

図面代用写真

(a)

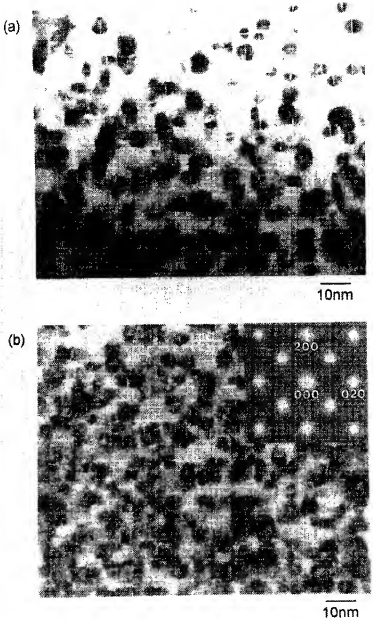


(b)



[Drawing 38]

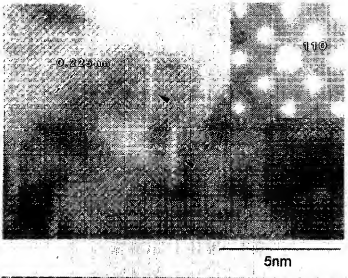
図面代用写真



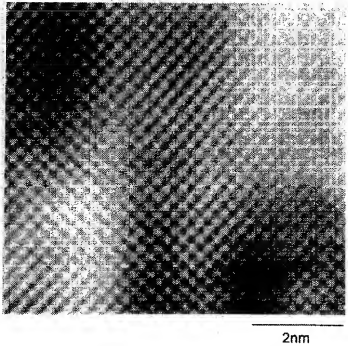
[Drawing 39]

図面代用写真

(a)



(b)



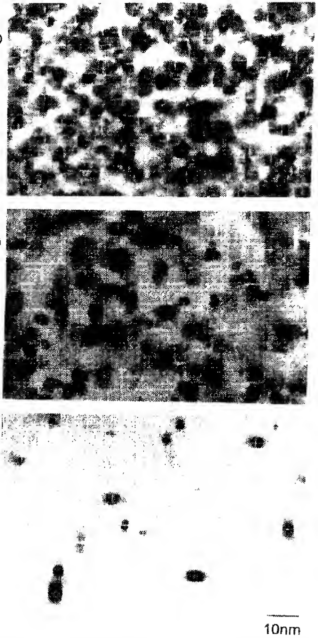
[Drawing 41]

図面代用写真

(a)
Hv~940

(b)
Hv~700

(c)
Hv~310



10nm